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ISOTOPIC EXCHANGE OF OXYGEN ON SILVER FILMS

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ABSTRACT   \ 6 ι 4 7

The authors analyze the oxygen bond on the surface of   /606*

silver by studying the isotopic exchange of adsorbed oxygen

with gaseous oxygen, and also by investigating homomolecular

exchange of oxygen. The adsorption kinetics were studied on

silver films condensed at room temperature and at -195°.

Tables are given for exchange rates in both reactions. It

is found that the adsorption-desorption mechanism is respon-

sible for both types of exchange.

Silver is used as a catalyst in selective oxidation of organic sub-

stances which is important in several processes, e. g. oxidation of ethylene

into ethylene oxide, methyl alcohol into formaldehyde, etc. In order to de-

termine the mechanism responsible for oxidative catalysis on silver, the state

of the adsorbed oxygen must be known. Many research workers have used varied

methods to study the state of oxygen on silver (references 1-10), but there

are considerable discrepancies on a number of basic problems, particularly

with regard to the form of the adsorbed oxygen.

In order to determine the nature of the oxygen bond on the surface of

silver, we studied the kinetics of both isotopic exchange of adsorbed oxygen

*Numbers given in margin indicate pagination in original foreign text.

with gaseous oxygen, and homomolecular isotopic exchange of oxygen. The ex-
change kinetics were studied in a static vacuum installation. Isotopic analy-
sis of the oxygen was done on an Mi-1305 mass spectrometer. Oxygen was ac-
cumulated in the ion source of the mass spectrometer through a glass capil-
lary directly connected to the reaction volume. Provision was made for both
continuous and periodic oxygen accumulation. The films were prepared in a
reaction vessel by vaporization from a helix of silver wire (99.99% Ag; wire
diameter 0.3 or 0.5 mm) heated by an electric current in a vacuum of 10^{-7} to
10^{-6} mm Hg.

The silver was condensed at $-195°$ or $20°$. The films were heated in
vacuum immediately after vaporization: films condensed at $20°$ were heated
for 3 hours at $250°$ or $300°$; films condensed at $-195°$ were first reheated to
room temperature, and then heated at $200°$ for 3 hours.

According to measurements of low-temperature krypton adsorption (refer-
ence 11), the surface area of the films condensed at $20°$ was 120-160 cm^2.
The film condensed at $-195°$ had an original area of 360 cm^2. Subsequent
heating of this film in oxygen to $250°$ reduced the surface to 300 cm^2 with
a final reduction to 250 cm^2 after prolonged heating under these same con-
ditions.

Oxygen enriched with isotope O^{18} (43%) was adsorbed on freshly prepared
films. A temperature of $200°$ was used for oxygen adsorption on films con-
densed at $-195°$, while oxygen was adsorbed at $250°$ on films condensed at $20°$.

The adsorption was basically completed 1½ hours after the beginning of
the experiment with only extremely slow adsorption taking place after this
period. Films condensed at $-195°$ adsorbed 0.7 monolayer in this length of
time, while those condensed at $20°$ adsorbed 2-3 monolayers. In calculating

the value of a single monolayer, it was assumed that $1.2 \cdot 10^{15}$ atoms of oxygen are needed to completely cover 1 cm^2 of silver surface.

After the adsorption was measured, the films were held for 12-40 hours at the adsorption temperatures indicated above and pressures of 0.04-0.15 mm Hg in enriched oxygen. In this case, a considerable reduction was observed /607 in the concentration of O^{18} in the gaseous oxygen. This shows that the films contained oxygen of the natural isotopic composition before adsorption. According to estimates based on reduction of the O^{18} content in the gaseous phase, the quantity of oxygen in the films before adsorption amounted to several monolayers. To all appearances, this oxygen was retained by the helix of silver wire in spite of preliminary degassing, and was absorbed during condensation of the silver.
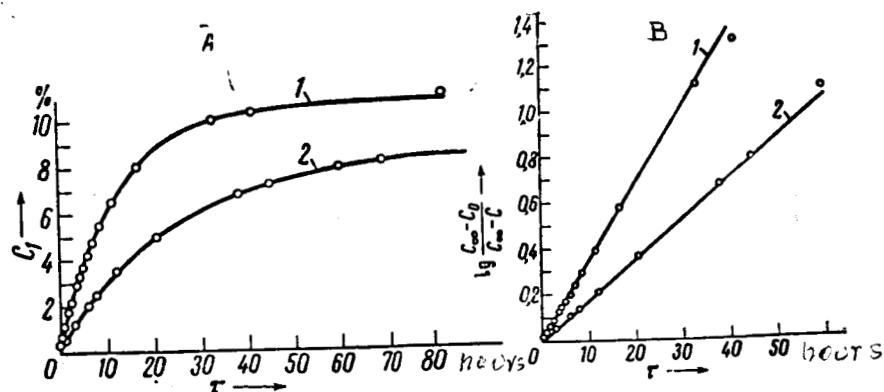

Fig. 1. Increase in O^{18} concentration in the gaseous phase at $200°$: 1--after holding at $200°$ (pressure $P = 0.12$ mm Hg, $N = 2.4 \cdot 10^{-6}$ mole, area $S = 360$ cm^2, $C_0^1 = 36.9\%$); 2--after holding at $250°$ ($P = 0.12$ mm Hg, $N = 2.4 \cdot 10^{-6}$ mole, $S = 300$ cm^2, $C_0^1 = 41.0\%$).

The oxygen was enriched by holding the films in oxygen.

Isotopic exchange with gaseous oxygen was carried out on the enriched

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films. This was done by pumping the enriched oxygen out of the reaction volume at room temperature and admitting oxygen of the natural isotopic composition. The reaction vessel was then placed in a furnace preheated to the experimental temperature, and isotopic exchange of adsorbed oxygen with gaseous oxygen took place. Isotopic analysis of the oxygen in the course of the experiment showed that exchange was almost continuous during the first hour. Our measurements were used for plotting curves to show the increase in $O^{18}O^{18}$ and $O^{16}O^{18}$ in the gaseous oxygen.

We used data from measurements of the rate of exchange during preliminary holding of the films in enriched oxygen to determine the O^{18} content in the adsorbed oxygen at the initial moment of the reaction. The rate of isotopic exchange after treatment of the films in heavy oxygen is $N(dC/d\tau)_{\tau_{fi}} = v(C_0' - C_{fi})$. At the beginning of exchange with natural oxygen, the rate is

$$N(dC/d\tau)_{\tau_0} = v(C_0' - C_0), \qquad (1)$$

where N is the quantity of gaseous oxygen in the system; τ is time; C is the fraction of O^{18} in the gaseous oxygen; C_0 is the fraction of O^{18} in the gaseous oxygen at the initial moment of isotopic exchange with natural oxygen; C_0' is the fraction of O^{18} in the adsorbed oxygen at the initial moment of isotopic exchange with natural oxygen; C_{fi} is the fraction of O^{18} in the gaseous oxygen after the preceding treatment; v is the rate of exchange. In previous calculations of the rates of exchange and the quantity of exchanged oxygen using the data of the first experiments, we took C_0' as equal to the O^{18} content in the initial enriched oxygen, which was considerably greater than the actual value of C_0'. Thus the values which we obtained for the indicated quantities were too low (reference 9). The kinetics of the isotopic exchange reaction were studied at 200° and 250° and 0.1-0.6 mm Hg. The increase in O^{18} concentration at 200°

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in the experiment with films condensed at -195° after adsorption and

holding in oxygen at 200° is shown in figure 1A (curve 1). After completion of

the reaction, the film was held in enriched oxygen at 250° and the kinetics of

the isotopic exchange were again measured at 200° (figure 1A, curve 2).

It is possible that the reduction in activity of the film is caused by

an increase in the oxygen content in the surface layers.

As evidenced in figure 1B, the kinetics of isotopic exchange at 200°

satisfy the equation of the first order

$$\frac{N \cdot N'}{N + N'} \ln \frac{C_\infty - C_0}{C_\infty - C} = v\tau, \tag{2}$$

where N' is the quantity of oxygen in the silver which takes part in the ex-

change; C_∞ is the fraction of O^{18} in the gaseous oxygen which corresponds to

isotopic equilibrium of the system; the other symbols have the same meanings

as in (1). Equation (2) is derived by integration of equation (1). From the

balance equation $NC_0 + N'C_0' = (N + N')C_\infty$, we find that the quantity N' of oxygen

in the film which takes part in the exchange is 2.8 monolayers in the first

experiment and 2.0 monolayers in the second. Thus the indicated quantity of

oxygen in the silver in these conditions is equivalent to the value in exchange

with gaseous oxygen which indicates uniformity with respect to energy.

The ratios of the initial rates of increase of the isotopic molecules

$O^{16}O^{18}$ and $O^{18}O^{18}$ in the experiments under consideration (figure 2) are equal

to 3.5 and 3.2 respectively which is close to the values which would be ob-

served for the case of desorption of equilibrium oxygen: at initial concen-

trations of O^{18} equal to 36.9 and 41.0%, the equilibrium ratios are equal to

3.4 and 2.9 respectively.

This ratio increases with the degree of exchange, but continues its cor-

respondence with desorption of the equilibrium gas.

This result indicates an adsorption-desorption mechanism with an extremely high rate of redistribution of the isotopic atoms in the adsorbed oxygen.
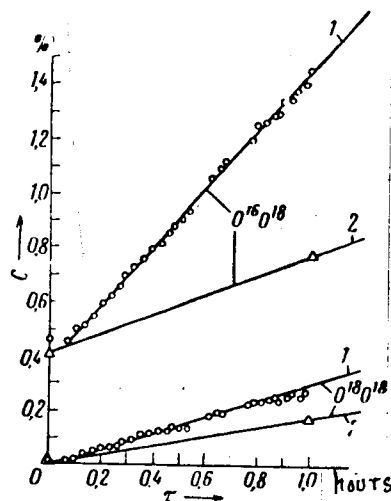

Fig. 2. Increase in concentrations of $O^{16}O^{18}$ and $O^{18}O^{18}$ at the beginning of experiments at 200° (the same experiments as in figure 1).
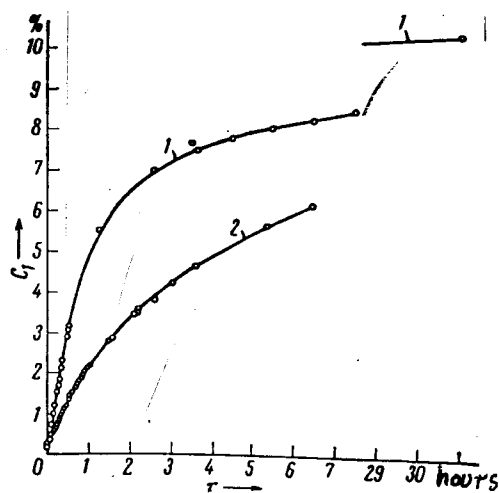

Fig. 3. Increase in concentration of O^{18} in the gaseous phase at 250°: 1--film condensed at -195° ($P = 0.12$ mm Hg; $N = 2.3 \cdot 10^{-6}$ mole; $S = 250$ cm^2; $C'_0 = 42.6\%$); 2--film condensed at 20° ($P = 0.11$ mm Hg; $N=2.3 \cdot 10^{-6}$ mole; $S = 120$ cm^2; $C'_0 = 33.6\%$).

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In exchange with gaseous oxygen at $250°$ (figure 3), an additional

1-2 monolayers of oxygen is observed, so that the total quantity of oxygen

taking part in the exchange is no less than 3-4 monolayers. Equation (2) does

not describe the reaction kinetics at this temperature since the additional

oxygen appearing in the reaction exchanges at a lower rate.

The specific rates of exchange are given in table 1. The data in this

table show that films condensed at $-195°$ do not differ from the other films

with respect to exchange when identical preliminary oxygen treatment is used.

The apparent activation energy of the reaction is 31 ± 2 Kcal/mole. The order

of the exchange with respect to oxygen pressure at $250°$ is equal to 0.3.

Homomolecular exchange of oxygen was studied on the films after ex-

periments on isotopic exchange. As a preliminary treatment, the films were

held at the reaction temperature in oxygen with the same content of O^{18} as in

the reaction mixture (a mixture of equal volumes of enriched and natural oxygen),

TABLE 1

Legend: a--temp. of condensed Ag vapor at film vaporization; b--temp. of pre-

liminary holding of the film in O_2; c--reaction of isotopic exchange of ad-

sorbed oxygen with gaseous oxygen; d--reaction of isotopic homomolecular ex-

change; e--reaction temperature; f--pressure, mm Hg; g--spec. rate of exchange,

mol/sec·cm²; h--apparent activation energy of the reaction, Kcal/mole.

a — Т-ра конденсации паров Ag при испарении пленки, °C	b — Т-ра предварительного выдерживания пленки в O_2, °C	c — Реакция изотопного обмена адсорбированного кислорода с газообразным				d — Реакция изотопного гомомолекулярного обмена			
		e — т-ра реакции, °C	f — давление, мм. рт. ст.	g — удельная скорость обмена, моль/сек×см²	h — кажущаяся энергия активации реакции, ккал/моль	т-ра реакции, °C	давление, мм рт. ст.	g — удельная скорость обмена, моль/сек-см	h — кажущаяся энергия активации, ккал/моль
—195	200	200	0,12	$4,4 \cdot 10^{-14}$		225	0,11	$0,94 \cdot 10^{-13}$	
—195	250	200	0,12	$1,8 \cdot 10^{-14}$	31	250	0,11	$4,9 \cdot 10^{-13}$	34
—195	250	250	0,12	$4,4 \cdot 10^{-13}$		250	0,10	$(3,1—3,7) \cdot 10^{-13}$	
20	250	200	0,11	$1,5 \cdot 10^{-14}$	31	250	0,10		29—32
20	250	250	0,11	$3,7 \cdot 10^{-13}$		300	0,10	$(4,1—4,7) \cdot 10^{-12}$	

until isotopic equilibrium was reached. The experiments were conducted at 225°, 250° and 300° at pressures of 0.1-0.7 mm Hg. The rates of exchange were calculated from an equation of the first order (reference 12).

As may be seen from the data of table 1, the initial rates of exchange for the reaction of isotopic exchange coincide with the reaction rates of the homomolecular exchange reaction. The activation energies for both reactions also coincide. The order of homomolecular exchange at 250° is also 0.3, as in the case of the isotopic exchange reaction.

Thus it may be concluded that both reactions take place according to the same mechanism--the adsorption-desorption mechanism. The result confirms the equality of desorption and exchange observed by Sandler and Hickam (reference 10).

The small value of the order indicates a considerable (>0.5) degree of covering under the conditions of our experiment. Nevertheless, a greater quantity of silver oxygen enters the exchange at 200° than can be found on the surface, and the fact that this oxygen is equal as regards exchange with the gaseous phase indicates that its activity is high.

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